



H₂S photodegradation by TiO₂/M-MCM-41 (M = Cr or Ce): Deactivation and by-product generation under UV-A and visible light

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ABSTRACT

M-MCM-41 molecular sieves (M = Ce or Cr) were prepared by a hydrothermal method and impregnated with TiO₂. The materials were characterized by XRD, N₂ adsorption–desorption, DRS and XPS. Their potential application to photooxidize H₂S in a wet gas stream was tested in a continuous flow reactor operating at a flow rate of 110 mL min^{−1} at 50% relative humidity and using 30 ppm_v of the pollutant. The photocatalytic efficiency using UV-A and visible light was compared to the activity of TiO₂/MCM-41 without heteroatoms incorporated into the MCM-41 structure. It was found that the incorporation of Ce did not improve the performance of TiO₂/MCM-41, but Cr-containing samples presented higher initial efficiency and were able to photooxidize H₂S without formation of SO₂ as a by-product, in contrast to the other prepared samples and to Degussa P-25 TiO₂. Moreover, no other gaseous by-product was detected. The isomorphic incorporation of Cr into the structure of MCM-41 followed by TiO₂ incorporation produced photocatalysts that presented good adsorption capacity and were much more active under visible light than under UV-light. This performance represents an important advantage for solar applications. Their photoactivity depended on the concentration of chromium; the highest efficiency was attained with samples with a Si/Cr ratio of 50. Finally, deactivation was observed as a consequence of sulfate accumulation on the surface of the catalyst and reduction of Cr⁶⁺.

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1. Introduction

Most research about heterogeneous photocatalysis uses TiO₂-anatase nanoparticles, which are known to absorb radiation below 387 nm (band-gap energy = 3.2 eV). TiO₂ may take advantage of just the UV-A range of the solar spectrum, which represents only 3–6% of the total solar radiation. In addition, the low photonic efficiency of TiO₂ [1] further limits its overall usefulness. As a result, artificial illumination is usually required and, consequently, the full potential of photocatalysis as a cheap and clean technology is not completely realized. Therefore, a great deal of attention has been devoted to design visible-light-activated materials to improve the photocatalytic systems [2] by approaches such as TiO₂ doping with metal ions [3], N [4], C [5] or S [6]; semiconductor coupling [7] or even the search for alternative TiO₂-free photocatalysts [8]. In this direction, mesoporous M41S molecular sieves

modified by incorporation of transition metals have been tested recently in heterogeneous photocatalysis.

MCM-41 is the most attractive member of the M41S family because of its hexagonal array of uniform pores with adjustable diameter (15–100 Å) and high surface area (typically > 1000 m² g^{−1}) [9]. The isomorphic incorporation of transition metals into the MCM-41 structure and impregnation with TiO₂ produces catalysts active under visible light [10]. In addition to acting as a support to control the dispersion and local structure of the active sites, molecular sieves have other useful properties such as the condensation effect for reactant gases or the shape selectivity due to the pore structure and restricted molecular-scale size [11]. Finally, the MCM-41 structure can enhance the interaction between TiO₂ and the transition metal, which is directly correlated to photoactivity. The good synergy between TiO₂ and Cr-MCM-41 has been recently demonstrated in the destruction of organic pollutants in aqueous phase [12]. The authors have proved the possibility of using this material also in gas phase photocatalysis in the elimination of thiophene [13]. The use of TiO₂/Cr-MCM-41 in gas phase eliminates the problem of Cr leaching and improves the environmental significance of these materials [14].

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The potential role of gas phase photocatalysis in the removal of malodorous and toxic compounds has been demonstrated by several authors [15–20]. One of the most targeted sulfur compounds to degrade is H_2S , a widespread chemical released as by-product of many processes, such as sour gas flaring, petroleum refining, pulp and paper manufacturing or wastewater treatment. H_2S has a very low odor threshold, 0.5 ppb_v [21], and the Threshold Limit Values-Short Term Exposure Limit (TLV-STEL) and Time-Weighted Average (TLV-TWA) are 10 and 15 ppm_v, respectively, in most European countries [22]. Although widely used, commercial H_2S removal techniques such as biofiltration and bioscrubbing [23], wet chemical scrubbing [24], incineration [25] and adsorption [26] are not optimal solutions. In fact, these techniques lack long-term stability, are non-destructive or require high chemicals and energy consumption. In contrast, the known advantages of photocatalysis make this technology very attractive. However, an important barrier to the full application of photocatalysis is the chemical nature of the pollutant and, consequently, of the reaction products. On one hand, most pollutants containing S (hydrogen sulfide, sulfur dioxide, dimethyl sulfide, dimethyl disulfide, carbon disulfide, carbonyl sulfide) or other heteroatoms such as N, P [27] or Si [28,29], are capable of promoting irreversible deactivation of the photocatalyst. For compounds containing sulfur, accumulation of sulfate as the final oxidation product may deactivate the photocatalyst [30,31]. On the other hand, a strategy to avoid deactivation could be limiting the photodegradation to reactions releasing gaseous oxidation products instead of depositing sulfate, but all gaseous sulfur compounds are toxic, corrosive and malodorous and therefore not recommended as final products of a treatment [32]. In our previous research with sol-gel TiO_2 and UV light, the feasibility of H_2S photocatalytic removal was confirmed [33]. Nevertheless, sulfate was found to accumulate on the surface deactivating the catalyst. Moreover, although Canela et al. did not find any reaction product besides sulfate [34] and Kataoka et al. found only a small amount of SO_2 attributed to sources other than photoreaction [35], Portela et al. have found, with both TiO_2 and $\text{TiO}_2\text{-ZrO}_2$ photocatalysts, that SO_2 was a reaction product [20]. The formation of sulfur dioxide has been observed during the photooxidation of other sulfur compounds. For instance, Nishikawa and Takahara observed its formation during tests with dimethyl sulfide [36].

In this study, we test the potential application of M-MCM-41 (M = Ce or Cr) molecular sieves impregnated with TiO_2 to destruct H_2S via photocatalysis using UV and visible light. The effect of the molecular sieve and the incorporated heteroatoms in the selectivity of the reaction and the nature of the catalyst deactivation is studied.

2. Materials and experimental

2.1. Synthesis of photocatalysts based on MCM-41

M-MCM-41 (M = Ce or Cr) molecular sieves were prepared using a hydrothermal method adapted from [37]. $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (Vetec, 97%) and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (Vetec, 99%) were used as metallic

precursors and tetraethylortosilicate (TEOS; Fluka, 99%) as source of silicon. In order to prepare samples with atomic ratio $\text{Si}/\text{M} = \infty$ (no heteroatom), 100, 50 and 25, the metallic precursors were added to a *N*-cetyl-*N,N,N*-trimethylammonium chloride solution (CTACl; Aldrich, 25%, w/w) under stirring. After 30 min, tetramethylammonium hydroxide solution (TMAOH; Fluka, 25%, w/w) was added dropwise under stirring. After addition of tetraethylortosilicate (TEOS; Fluka, 99%), the resulting mixture was stirred for 1.5 h. The molar ratio $\text{SiO}_2\text{:CTACl:TMAOH:H}_2\text{O:M}$ (Cr_2O_3 or CeO_2) was 1:0.40:0.26:25:*x* (where *x* = 0, 0.01, 0.02 or 0.04). The final mixture, with pH values between 11 and 12, was treated under autogenous pressure without stirring at 135 °C for 14 h in a steel autoclave internally lined with Teflon. The resulting solids were filtered, washed with distilled water until pH 7 was reached, and dried in an oven at 90 °C for 12 h. The template was removed by calcination under N_2 flow at 540 °C for 1 h (heating rate of 2 °C min⁻¹) followed by 5 h under airflow at the same temperature.

The resulting materials were impregnated with 20 wt% of TiO_2 obtained by hydrolysis of titanium(IV) isopropoxide (Aldrich, 97%). The molecular sieve (typically 1.0 g) was suspended in 80 mL of isopropyl alcohol (Synth, p.a.) and the proper amount of $\text{Ti}(\text{OPri})_4$ was added to achieve 20 wt% of TiO_2 . The suspension was stirred at ambient temperature and 1 mL of water was added dropwise. After 1 h the solvent was evaporated by heating at 50 °C. The samples were dried in an oven for 1 h at 90 °C and calcined at 450 °C under airflow for 4 h.

In Table 1 are listed the different prepared samples (the number in brackets is the Si/M ratio) together with the sample P25- SiO_2 , prepared for comparative purposes by mixing commercial SiO_2 (Merck) and TiO_2 (Degussa P-25). When the samples have been used in photocatalytic tests with either visible or ultraviolet-A radiation the suffix “VIS” or “UV-A” was added.

2.2. Characterization of synthesized photocatalysts

This study used N_2 physisorption to determine surface area and pore size distribution with a Quantachrome Autosorb 1C. All samples were degassed for 1 h at 300 °C under vacuum before analysis. Surface areas and pore size distributions were determined using BET ($P/P_0 = 0.05\text{--}0.30$) and BJH methods, respectively, both through Autosorb for Windows[®] software, version 1.24. Diffuse reflectance spectra (DRS) in the range of 200–800 nm were recorded by a Varian spectrophotometer equipped with ISR1200 integrating sphere attachment using BaSO_4 as reference. X-Ray Diffraction analysis was performed by means of an X'Pert Pro PANalytical automatic diffractometer, using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154$ nm) with a Ni filter. Low angle measurements were performed in the 2θ range from 0.4° to 8° with a step size of 0.02° and a step time of 20 s.

X-ray photoelectron spectra (XPS) were obtained with a VG Escalab 200R spectrometer fitted with a monochromated Mg $\text{K}\alpha$ radiation ($h\nu = 1253.6$ eV) 120 W X-ray source and a hemispherical electron analyzer. The powdered samples were placed on a sample rod and introduced in a pre-treatment chamber to be degassed at

Table 1
Results of textural and structural characterization of the photocatalysts

Sample	Si/M	TiO_2 (%)	BET (m^2/g)	Pore size (Å)	Pore volume (cm^3/g)	Unit cell parameter a_0 (Å)	TiO_2 size (nm)
P25- SiO_2	∞	20	51	–	–	–	23.0
$\text{TiO}_2/\text{MCM-41}$	∞	20	1068	22	0.54	49	13.3
$\text{TiO}_2/\text{Ce-MCM-41}(100)$	100	20	724	24	0.64	43	14.2
$\text{TiO}_2/\text{Ce-MCM-41}(50)$	50	20	542	23	0.57	48	8.9
$\text{TiO}_2/\text{Cr-MCM-41}(100)$	100	20	823	24	0.62	51	7.0
$\text{TiO}_2/\text{Cr-MCM-41}(50)$	50	20	557	29	0.60	52	6.9
$\text{TiO}_2/\text{Cr-MCM-41-(25)}$	25	20	316	18	–	–	–

25 °C and 10^{-3} Pa for 5 h prior to their transfer to the analysis chamber. Residual pressure during data acquisition was maintained below 3×10^{-7} Pa. The energy regions of the photoelectrons of interest (Cr2p, Ti2p, Si2s, O1s, S1s), were scanned several times to provide an acceptable signal-to-noise ratio. Accurate binding energies (± 0.2 eV) were determined by referring to the C1s peak at 284.9 eV.

2.3. Photocatalytic activity tests

The photocatalytic tests were performed in a steel tubular reactor ($d_{\text{int}} = 18.2$ mm) illuminated by an internal 8 W lamp placed in axial position ($d_{\text{ext}} = 15.2$ mm). OSRAM L8W/954 was used for tests made with visible light (emission maximum at around 460, 540 and 615 nm) and PHILIPS TL8W/05 FAM for tests made with UV light (emission maximum at 365 nm). 200 mg of photocatalyst were placed in the thin annular volume between the lamp and the reactor wall (thickness: 3 mm). The catalyst occupied a length of 10 mm and was held in place by plugs of glass wool. A continuous inlet gas stream with a flow rate of 110 mL min^{-1} , 30 ppm_v of H₂S and 50% relative humidity at 30 °C entered the reactor. This procedure implied a residence time of 0.43 s and a space time (calculated as catalyst load to molar flow rate ratio) of $8 \times 10^{10} \text{ mg S mol}^{-1}$. H₂S was supplied from a certified H₂S/N₂ cylinder (Air Liquide) and diluted with wet air. The desired concentrations of pollutant, H₂O and O₂ ($20 \pm 1\%$) in the air were attained by means of liquid and gas mass flow controllers, in a system that has already been reported [33]. The analysis of the gaseous compounds was performed using a Micro-GC Varian CP-4900 equipped with a micro thermal conductivity detector (μ -TCD) and a CP-PoraPlotQ column (10 m \times 0.15 mm). The concentration of the continuous inlet gas stream was measured in by-pass until stabilization before each run. The gas stream was then passed through the reaction system in dark conditions. The lamp was turned on only when the adsorption equilibrium was reached (the H₂S concentration was higher than 95% of the by-pass value).

3. Results and discussion

3.1. Characterization of synthesized photocatalysts

3.1.1. XRD studies and N₂ adsorption isotherms

Low angle XRD patterns of these materials showed a peak at 2θ values of about 2° in all cases, as shown in Fig. 1 for some representative samples. This peak can be indexed to the (1 0 0) reflection of the hexagonal array of pores characteristic of MCM-41

phase [38]. However, the relatively low intensity of this feature, coupled with the absence of the weaker high-index peaks, indicates that the MCM structure was not completely ordered, and therefore the existence of some amorphous domains in our samples was highly likely. In contrast with other studies [39,40] the incorporation of Cr or Ce is not clearly detrimental for the crystallinity of our samples because, as displayed in Fig. 1, the intensity of the (1 0 0) peak presents similar or higher intensity for samples containing metals than for the pure siliceous molecular sieve. The unit cell parameter of the hexagonal cell, a_0 , can be calculated from the spacing of the (1 0 0) planes, d_{100} , according to the equation $a_0 = 2d_{100}/\sqrt{3}$ [40]. The results obtained for these samples are summarized in Table 1. The data indicate that the incorporation of Cr slightly increased the unit cell, while Ce addition had the opposite effect. Although the increment of the M–O distance with respect to Si–O is expected to yield an increment of a_0 , the opposite tendency has been observed as well [39], as specific synthesis conditions may affect wall thickness.

Meanwhile, TiO₂ incorporation was studied by high angle (20 – 80° 2θ) XRD measurements. The obtained results revealed the formation of TiO₂-anatase, whose pattern is overlapped with the broad amorphous halo of SiO₂ at about 23.4° . However, there is no obvious indication of the presence of other metal oxides. The crystallite size of TiO₂ for samples with and without Cr or Ce estimated by the Scherrer equation was summarized in Table 1. These results show that Cr incorporation results in anatase crystals of smaller diameter, which could be caused by an easier nucleation on the metal-modified surface of the molecular sieve.

The N₂ physisorption isotherms are of type IV, according to IUPAC classification, a typical pattern of mesoporous structures [41]. All samples exhibited complementary textural- and framework-confined mesoporosity, which was evidenced by the presence of two separate and well-defined hysteresis loops. Isotherm profiles were not modified by TiO₂ impregnation. The formation of larger pores in samples containing chromium or cerium was associated to the formation of defects (or distortions) in the molecular sieve structure (Table 1). The surface area decreased with the amount of chromium and cerium in the samples. The same trend has been reported in the literature [42].

3.1.2. Diffuse reflectance spectroscopy–UV–vis

Fig. 2 shows UV–vis spectra of Cr-MCM-41 and Ce-MCM-41 impregnated with 20 wt% TiO₂. Chromium-containing materials showed absorption beginning at approximately 600 nm, while samples without chromium absorbed light only in the UV-range. The presence of the heteroatom apparently reduced the band-gap

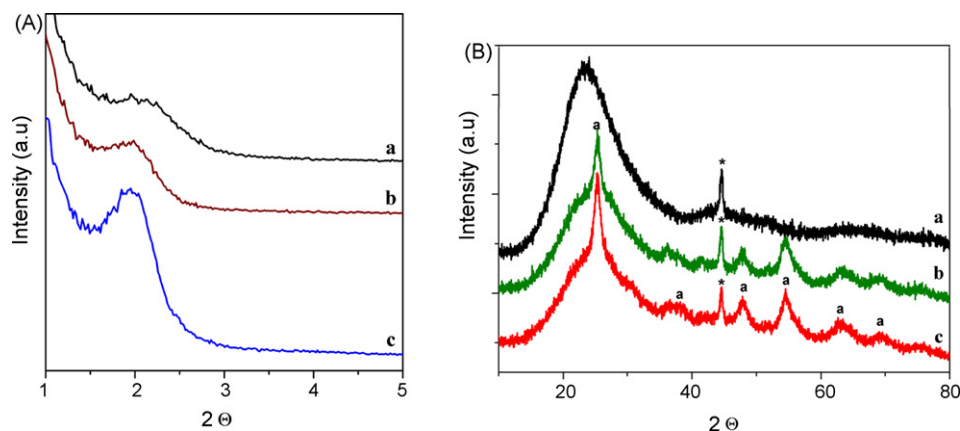


Fig. 1. XRD patterns at low (A) and high (B) angle of the samples (a) MCM-41, (b) TiO₂/Cr-MCM-41(100) and (c) TiO₂/Cr-MCM-41(50). The star marks a peak of the sample holder, while “a” stands for the anatase peaks.

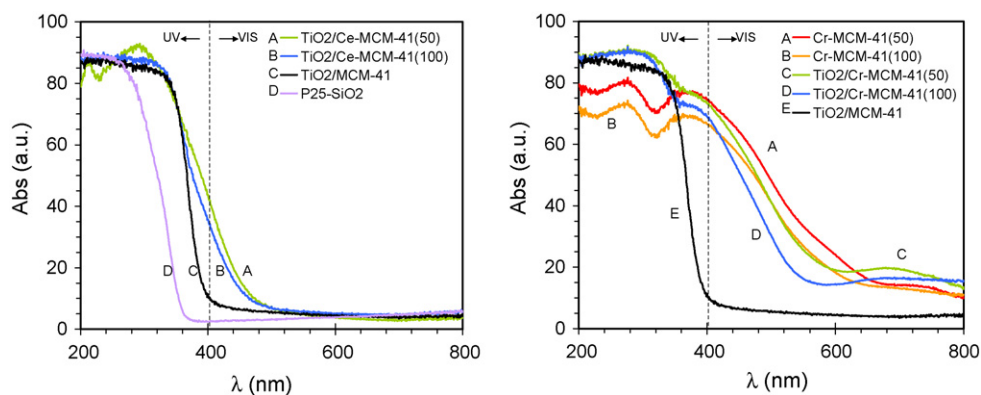


Fig. 2. DRS-UV-vis spectra of the molecular sieves modified with Ce (left) and Cr (right).

energy from the 3.2 eV value found for pure TiO₂ to ≈ 2.0 eV. These results demonstrate that the synthesized materials have a great potential as photocatalysts capable of using solar light. DRS spectrum of calcined Cr-MCM-41(100) has two intense bands at 275 and 390 nm, attributed to $O(2p) \rightarrow Cr^{6+}(3d^0)$ charge transfer of chromate (CrO_4^{2-}) species, that indicate chromium oxidation to Cr(VI) during calcination [43,39]. Moreover, d–d transition of Cr^{5+} occurs in the same spectral region. The band at 440 nm may be assigned to octahedral Cr^{3+} ions which indicate the presence of Cr^{3+} in the calcined sample, even under calcination temperatures of 630 °C. Rodrigues et al. detected Cr^{3+} species on Cr-MCM-41 [38]. The band at 440 nm may also be attributed to the forbidden charge transfer band of dichromate species [44]. In our study, such process was difficult to observe due to the overlap with TiO₂ adsorption band, after the impregnation. A band at ≈ 350 nm confirmed the formation of anatase TiO₂ in chromium and cerium-containing materials. Band coincidence between TiO₂ and chromate species indicates that the absorption in the range of 370–500 nm could be related to a heterojunction of titania and chromium. The spectra of chromium-containing samples showed an absorption band around

700 nm in the red region of the electromagnetic spectrum assigned to d–d transitions described as $^4A_{2g}(F) \rightarrow ^4T_{2g}(F)$ from Cr^{3+} in octahedral coordination [45]. The cerium-containing materials showed an absorption band below 300 nm attributed to the electronic transition from oxygen to cerium for a tetra-coordinated Ce^{4+} ($O^{2-} \rightarrow Ce^{4+}$) [42]. The absorption in the visible region was very weak and no absorption was detected above 500 nm.

3.1.3. X-ray photoelectron (XPS) analysis

Samples with different Cr content were analyzed by X-ray photoelectron spectroscopy. The energy regions for Cr2p, Ti2p, Si2p, O1s and S1s were analyzed for all the samples. The Ti2p_{3/2} region showed a band centered at 458.5 eV with a satellite peak at 464.2 eV characteristic of TiO₂-anatase. The binding energy for Si2p core level was found at 103.3 eV, corresponding to SiO₂. In Fig. 3a and b the Cr2p and O1s spectra for samples with atomic ratio Si/Cr = 100 and Si/Cr = 25 are displayed and the surface atomic ratios calculated for Cr-containing samples are collected in Table 2. The analysis of the Cr2p_{3/2} region showed the presence of two different Cr species or chemical states on the catalysts surface

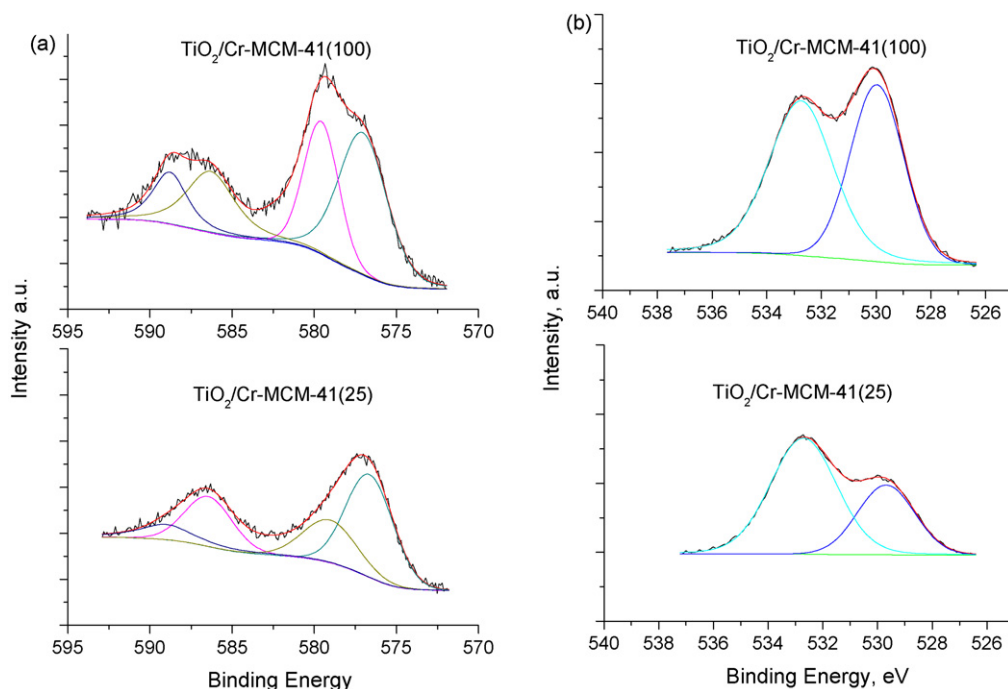


Fig. 3. XPS spectra of the core levels for TiO₂/Cr-MCM-41 samples with different Cr loading (a) Cr2p (b) O1s.

Table 2

Surface atomic ratios calculated for Cr-containing samples

	Cr/Ti	Cr ³⁺ /Cr total (%)	S/Ti
TiO ₂ /Cr-MCM-41(100)	0.34	60	–
TiO ₂ /Cr-MCM-41(100)VIS	0.16	75	0.05
TiO ₂ /Cr-MCM-41(100)UV-A	0.12	94	0.06
TiO ₂ /Cr-MCM-41(25)	0.45	67	–
TiO ₂ /Cr-MCM-41(25)VIS	0.42	77	0.13

with maxima centered at 576.6 and 579.0 eV, corresponding to Cr³⁺ and Cr⁶⁺ species, respectively. The presence of these two species has been observed previously with other supports [46]. The deconvolution of the O1s spectra showed two bands, centered at 532.7 and 529.7 eV. The former corresponded to oxygen from SiO₂ [47] and the latter assigned to the combination of oxygen species from TiO₂ and CrO_x [48]. As expected, higher SiO₂ content in TiO₂/Cr-MCM-41(100) resulted in higher contribution of the O1s band centered at 532.7 eV. The sample with Si/Cr = 25 presented the highest Cr/Ti ratio and also a greater amount of Cr³⁺, in agreement with Sun et al., who found that samples with smaller Si/Cr ratio contained mixed oxidation states and therefore lower Cr⁶⁺/Cr_{total} [14]. Nevertheless, considering the Cr/Ti ratio calculated by XPS and the Si/Cr theoretical ratio, the results suggest the formation of extra-framework Cr, probably as Cr₂O₃, reducing the metal dispersion on TiO₂/Cr-MCM-41(25).

In order to verify whether there was any influence of the irradiation and radiation type on the oxidation state of superficial species, XPS analyses of some samples were performed after reactions using visible and UV-A lamps (Fig. 4). A band centered at 168.7 eV was detected now in the S1s spectra. According to the literature, this band was assigned to sulfate species [49]. A dependence of the S/Ti ratio with the Cr content in the sample was found (Table 2). On the other hand, the photocatalytic reaction promoted an increase of the Cr³⁺/Cr_{total} ratio in all the studied cases, due to the reduction of Cr⁶⁺ to Cr³⁺. Moreover, UV-A radiation, more energetic than visible radiation, practically caused the total reduction to Cr³⁺. The decrease of the Cr/Ti ratio after the

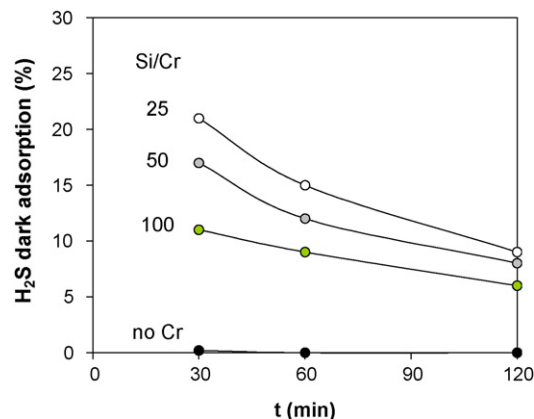


Fig. 5. Adsorption of H₂S in the dark as a function of chromium content. Si/Cr = ∞ (●), 100 (●), 50 (●) and 25 (○).

catalytic test was probably due to the deposition of sulfate over the Cr species (Fig. 5).

3.2. Adsorption capacity of the samples

The adsorption capacity of the different catalysts under dynamic conditions in wet air was measured before the photocatalytic tests. The H₂S adsorption capacity was very low when no heteroatom was incorporated into the structure of the molecular sieves. However, the adsorption capacity improved with the amount of chromium (Fig. 4), despite a decrease in the surface area. Previous studies reported the use of hydrogen sulfide to reduce Cr(VI) to Cr(III) species [50]. Therefore, considering that these samples contain a significant amount of Cr⁶⁺, as revealed by XPS analysis, H₂S could initially reduce part of the chromate present in Cr-containing molecular sieves. Nevertheless, this process does not lead to the total reduction of the chromate species present in the samples, as the study of the used catalysts indicates. This fact could

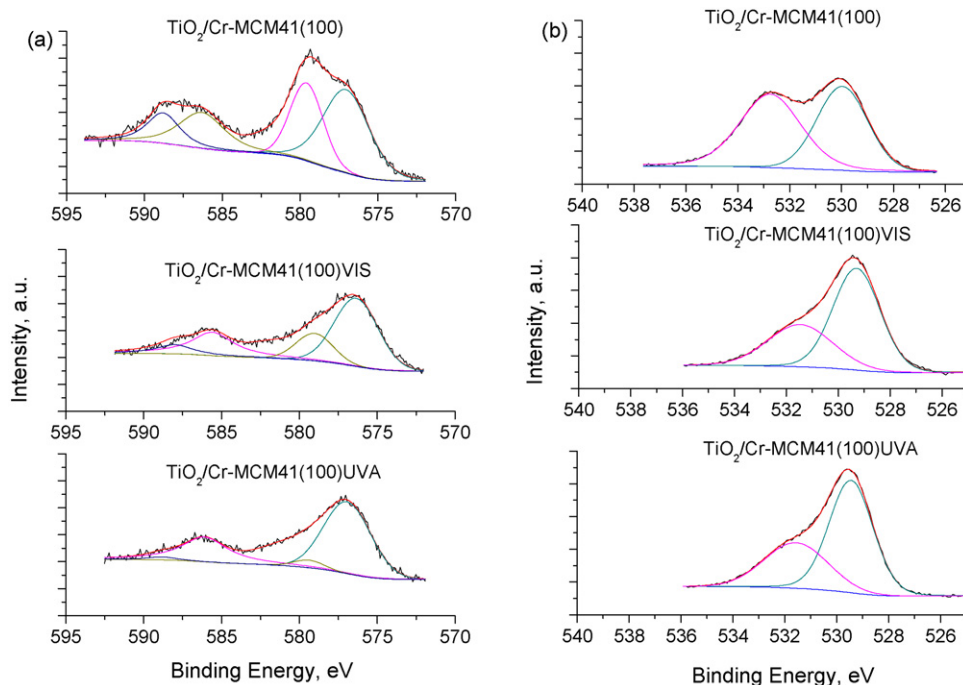


Fig. 4. XPS spectra of the core levels for fresh and used samples: (a) Cr2p and (b) O1s.

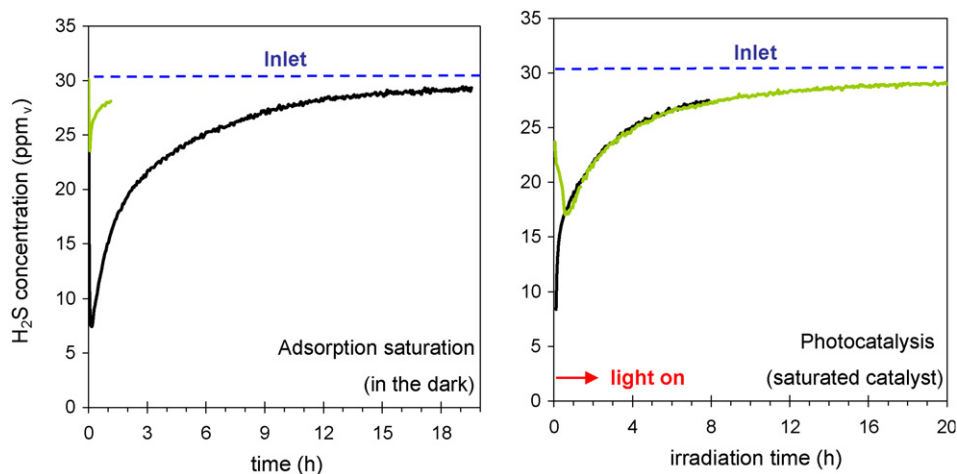


Fig. 6. Behavior of TiO₂/Cr-MCM-41(50) sample in the dark (left) and during irradiation with UV-A light after saturation (right) with wet (●) or dry (●) inlet gas streams.

be related with the presence of different monochromate/poly-chromate species in the molecular sieve after calcination [44,13].

For comparative reasons, one test in the absence of humidity has been performed. The results confirmed the competition for adsorption sites between water and hydrogen sulfide, since H₂S adsorption capacity in the dark dropped drastically when humidity was present in the continuous gas stream (Fig. 6, left). Once the catalyst surface was saturated, it was irradiated in order to eliminate H₂S photocatalytically. The humidity did not seem to affect the photocatalytic activity (Fig. 6, right).

3.3. Photocatalytic activity

A blank test (without catalyst) demonstrated the absence of homogeneous photolysis of H₂S. In Fig. 7 a typical photocatalytic test is shown. When a constant concentration by-passing the reactor is reached, the polluted wet gas stream is passed through the reactor in the dark, until the adsorption drops below 5% of the H₂S in the feed. Then the light is turned on. Around 30 min, in the case of the UV-A-lamp, or 45 min, in the case of the visible-lamp, are necessary to reach the new adsorption equilibrium, due to the progressive temperature increase produced during the lamp initialization, which causes water and H₂S desorption.

3.3.1. Photocatalytic activity with UV-A light

Fig. 8 shows the evolution of the photoactivity during 6 h of UV irradiation of TiO₂/M-MCM-41 molecular sieves (M = Ce or Cr, Si/

M = 50 and 100) compared to the TiO₂-MCM-41 molecular sieve (without heteroatom) and to a mixture of commercial SiO₂ and TiO₂ with the same TiO₂ content (20%, w/w). The latter presented the highest conversion, 80%, and no deactivation occurred within 3 h. Despite the higher surface area of the molecular sieves, P25-SiO₂ was more efficient in the degradation of H₂S than TiO₂ impregnated on MCM-41. The higher efficiency in H₂S degradation of P-25 from Degussa can be explained by the synergic effect of anatase and rutile allotropic forms present in this material, an effect widely described in the literature [51,52], while TiO₂ added to MCM-41 is present only in the anatase form.

Among the molecular sieves, the one without heteroatom converted 33% of the H₂S and no deactivation occurred during 24 h; the addition of Ce did not seem to improve this performance. The incorporation of Cr at the adequate concentration (Si/Cr = 50) had two different effects: the initial conversion rate was enhanced and the deactivation was faster. This result can be adequately explained by observing the formation of SO₂ during the photo-reaction (Fig. 9), which is the only gaseous product detected during H₂S photocatalytic degradation [20].

With P25-SiO₂ most of the H₂S was converted into SO₂, which was desorbed and released with the outlet gas stream. Therefore, deactivation did not occur, but the degradation product into which the pollutant was converted is both toxic and corrosive. On the other hand, during tests with TiO₂/Cr-MCM-41 samples, no gaseous products containing sulfur were detected. Sulfate or

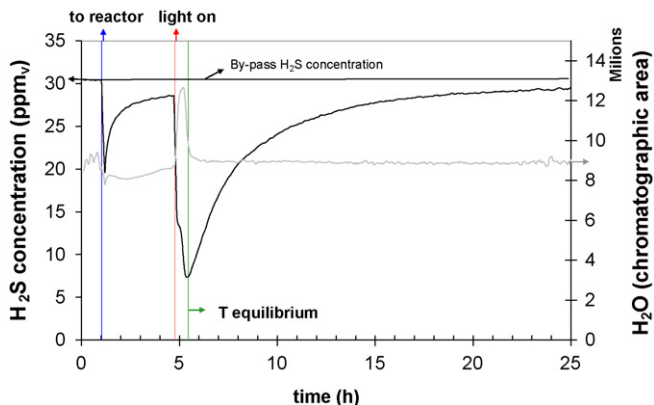


Fig. 7. H₂S (●) and water (●) during visible light test with TiO₂/Cr-MCM-41(50) sample.

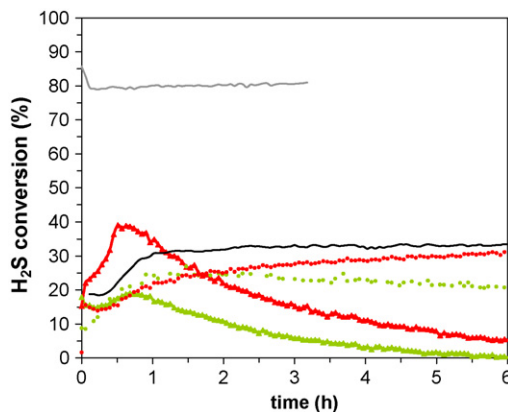


Fig. 8. H₂S conversion over time under UV-A light for P25-SiO₂ (—), TiO₂/MCM-41 (—), TiO₂/Ce-MCM-41(100) (····), TiO₂/Ce-MCM-41(50) (····), TiO₂/Cr-MCM-41(100) (····) and TiO₂/Cr-MCM-41(50) (····).

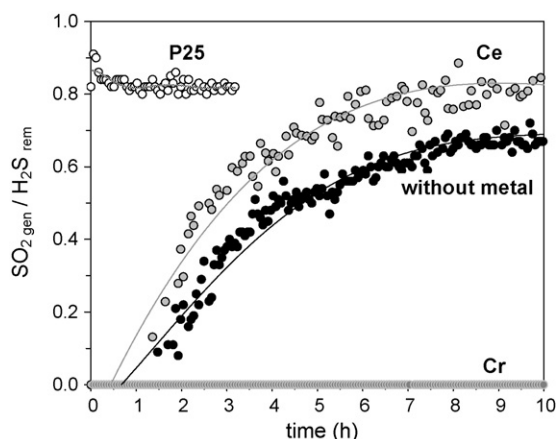


Fig. 9. SO_2 generation during H_2S UV-photooxidation with $\text{TiO}_2/\text{MCM-41}$ (●), $\text{TiO}_2/\text{Ce-MCM-41(100)}$ (●), and P25-SiO_2 (○). During tests with $\text{TiO}_2/\text{Cr-MCM-41(100)}$ no SO_2 was detected under neither UV light nor visible light.

elemental sulfur, the most likely reaction products, would accumulate on the surface of the photocatalyst covering the active sites and, therefore, lead to a progressive loss of activity. In the case of $\text{TiO}_2/\text{MCM-41}$ and $\text{TiO}_2/\text{Ce-MCM-41}$, SO_2 appeared in the outlet gas stream after some minutes of reaction, corroborating previous results on the same subject [20].

In addition to the deactivation caused by products accumulation, the influence of Cr^{6+} reduction on this process, according to XPS results, must not be ignored. Sun et al. have reported that $\text{TiO}_2/\text{Cr-MCM-41}$ catalysts deactivate gradually during 4-chlorophenol degradation under visible light due to Cr^{6+} reduction [14]. These authors have also found that reduced chromium in the photocatalyst can be completely reoxidized by heating the catalyst at 450°C for 3 h. Davydov et al. have found the same kind of deactivation and confirmed the progressive reduction of Cr^{6+} to Cr^{3+} and Cr^{2+} [10].

3.3.2. Photocatalytic activity with visible light

Samples containing Cr show light absorption above 400 nm (see Fig. 2), indicating that they might show photocatalytic activity under visible light. Fig. 10 shows the photoactivity of the molecular sieves with Si/Cr ratios of ∞ (no Cr), 100, 50 and 25. As expected, the sample without chromium was unable to photodegrade H_2S

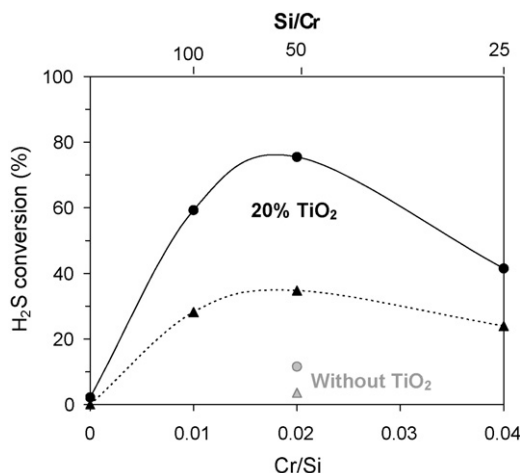


Fig. 10. H_2S conversion under visible light for MCM-41 with 20% TiO_2 (black) and without TiO_2 (gray) after 45 min (○) and 180 min (△) of illumination.

under visible light, while samples containing chromium were very active photocatalytically, 2–3 times more active than under UV-A light. Nevertheless, it has been found that the sample with Si/Cr = 50 was more active than the samples with Si/Cr = 25 or 100. This result indicates that there is an optimal amount of chromium for these photocatalysts. According to XPS results, the sample with higher metal loading presented higher S/Ti ratio, indicating that probably the extra-framework Cr_2O_3 favored the formation of sulfate and, in addition to the lower surface area and higher content of Cr^{3+} , the faster catalyst deactivation. Cr-MCM-41(50) sample showed very low conversion of H_2S , which was attributed to the fast reduction of Cr^{6+} [50]. Davydov et al. have shown that the interaction of Cr^{6+} and TiO_2 is essential for the activity of the photocatalyst, because it allows the charge transfer transition $\text{Cr}^{6+}=\text{O}^{2-} \rightarrow (\text{Cr}^{5+}-\text{O}^-)^+$, which is promoted by visible light [10]. Therefore, Cr^{5+} species can probably donate an electron to the neighboring TiO_2 . Meanwhile, the O^- of the photoexcited chromate species can withdraw electrons from the TiO_2 particles, leaving an oxidant hole in the valence band during the decay process.

Ce-containing samples impregnated with TiO_2 did not show any activity in the visible light, as expected due to the scarce absorption in the visible range (see Fig. 2).

3.4. Discussion

H_2S was converted either into sulfate, which accumulated on the surface deactivating the catalyst, or as previous studies [33] into both sulfate and SO_2 , toxic and corrosive compound which was desorbed and released with the outlet gas stream, depending on the incorporation of Cr or not to the molecular sieves. In the first case, the reaction may take place using visible light at even higher reaction rate than using UV-A light, which enables the reaction activation by solar energy.

$\text{TiO}_2/\text{M-MCM-41}$ samples are equally active in the presence or absence of water vapor, which may be related to the higher surface area and to the large amount of Si-OH available in the molecular sieves than the supported TiO_2 used in previous studies, where higher initial photoactivity and faster deactivation of the catalyst were observed with dry inlet gas streams [20] compared to streams containing water vapor [33].

The presence of Cr^{6+} on the catalysts was essential to carry out the photocatalytic reaction, but low Cr concentration ($\text{Si/Cr} \geq 50$) favors the conversion. Cr^{6+} was reduced to Cr^{3+} during the photocatalytic process, according to XPS results before and after the photocatalytic test, probably by the electrons accumulated on the catalyst surface. Therefore, the increase of Cr^{3+} concentration was one reason for the catalysts deactivation. According to Rodrigues et al., during the degradation of trichloroethylene, $\text{Cr}^{6+}/\text{Cr}^{5+}$ were the only photospecies susceptible to absorb visible-wavelength photons, whereas with UV light Cr^{3+} species were also active [38]. Davydov et al. [10] observed that Cr^{6+} was essential for the reaction using visible light, since its fully reduced form did not exhibit any photoactivity, but the role of Cr^{3+} was not clear, even if the deactivated catalysts were rich in Cr^{3+} .

The catalysts deactivation was mainly caused by the reduction of Cr^{6+} to Cr^{3+} and the blockage of active sites due to the accumulation of sulfate on the catalysts surface. Nevertheless, this deactivation may be reversible. Sun et al. pointed out that the reduced chromium in 25% $\text{TiO}_2/\text{Cr-MCM-41}$ can be reoxidized to Cr^{6+} by calcination at 450°C and under this circumstance the catalyst regeneration would be achieved [14]. We have analyzed a 20% $\text{TiO}_2/\text{Cr-MCM-41}$ deactivated sample by thermogravimetry-mass spectrometry (TG-MS) and the formation of sulfur species (SO and SO_2) with a maximum at 460°C indicates that sulfate may be decomposed by calcination as well.

4. Conclusions

MCM-41 molecular sieves with incorporated Cr or Ce and impregnated with TiO₂ (20%, w/w) showed high efficiency to photooxidize H₂S in gas phase.

Among the prepared photocatalysts tested, the highest H₂S conversion was obtained by the use of TiO₂/Cr-MCM-41 and visible light. TiO₂/Cr-MCM-41 degraded H₂S with either UV- or visible light and did not generate any other toxic gaseous product, such as SO₂, which is a problem when the samples without Cr incorporation or TiO₂ P-25 from Degussa are used. Nevertheless, the catalyst deactivated with time due to the reduction of Cr⁶⁺ to Cr³⁺ and the blockage of active sites by sulfate accumulation on the surface. The photoactivity depended on chromium concentration and the optimal Si/Cr ratio was found to be 50.

The incorporation of Ce to the structure of the molecular sieves has neither improved their performance, nor avoided SO₂ formation or extended the activity to the visible range.

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